

# Modified carbon-containing electrodes in stripping voltammetry of metals

## Part I. Glassy carbon and carbon paste electrodes

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**Abstract** Papers dealing with modified electrodes made of carbon materials and composites for use in stripping voltammetry of metals have been reviewed. The review consists of two parts, of which the first considers applications of modified glassy carbon and carbon paste electrodes, while the second describes diverse modified carbon-containing composite and microscopic electrodes. Information about modifiers, electrode modification methods, conditions, and limits of detection of elements in different materials has been tabulated. The review covers 550 papers published in Russia and abroad between 1990 and the first half of 2007.

**Keywords** Modified electrodes · Glassy carbon · Carbon paste electrodes · Stripping Voltammetry · Metal ions determination

### Introduction

Voltammetry is one of the most universal methods of electroanalytical chemistry, which is widely used as a technique for measurement of concentrations of substances and as a tool for analysis of their properties. The growing number of papers concerned with problems and urgent issues of voltammetry is indicative of the increasing interest among chemists to this method. The general status and future trends of voltammetry and electrochemical sensors are described in the reviews [1–7]. A priority line of its

development that follows from the analysis of those papers is the creation, the study and the use of new electrodes, electrochemical sensors [8], transducers, and detectors for automated, flow-through, and “field” analysis. This is because the electrochemical signal is formed by processes taking place on the electrode surface. Therefore, the condition of the electrode surface, which depends on the origin, the defect content, and the mechanical inhomogeneity of the material, determines many significant quantitative characteristics of electrochemical measurement systems. Required electrochemical properties of the electrode can be obtained if its surface is modified purposefully. Therefore, the modification and the “molecular design” of the transducer surface and the formation of grafted layers on solid surfaces constitute an actively developing new area of investigation. Problems of the chemical modification of solid surfaces, specific and regular features of the modifier attachment to various solid matrices, and examples of practical applications of chemical sensors (modified electrodes) are overviewed in the papers [9–21].

Over a period of years, the development of the voltammetric method was connected with metal, primarily mercury, electrodes. But mercury is an extremely toxic material. This element presents the first-rate hazard leading to severe poisoning and heavy diseases. For this reason, some countries (USA, Japan, EC) have declared a moratorium on the use of mercury in storage batteries, lamps, thermometers, pesticides, etc. Electrodes made of nontoxic materials also tend to smoothly force out mercury electrodes in electroanalysis. As an alternative to toxic mercury electrodes, electrodes of a nontoxic “dental” amalgam ( $\text{Ag}_2\text{Hg}_3$  with the surplus silver; [22, 23]) have been developed and used for measurements of heavy metals. Carbon materials (CMs) possessing some attractive features [24, 25] are widely used as mercury-free current-conducting

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electrode materials. *Firstly*, depending on the CM type, the character of the electrical conduction can change from the metal to the semiconductor conduction suggesting broad potentials for a wide range of capacitive, adsorption, catalytic, and kinetic properties. *Secondly*, the carbon surface can adsorb a variety of compounds by both the nonspecific physical sorption and the specific chemisorption with a functional coating, which can be formed either under the forced action of reagents or due to the presence of native functional groups resulting from a thermomechanical treatment of the material [25, 26]. *Thirdly*, the complexation capacity of carbon materials is higher than that of metals. *Fourthly*, CMs can form strong covalent bonds with some surface modifiers favoring the development of modified electrodes. *Fifthly*, the carbon surface is electrochemically inert over a wide interval of potentials. All these features predetermine the use of diverse carbon materials in electroanalysis. Glassy carbon, pyrolytic graphite, carbon glass-ceramics, impregnated graphite, carbon fibers, filaments, cloths, gauzes, and composite materials serve as the electrode material. The properties of CM electrodes, their specific features and drawbacks, and applications in voltammetric measurements of substances are described in the Russian reviews published in 1988 and 1990 [27, 28]. The present overview covers papers published in Russia and abroad since 1990. To narrow the borders of an extensive literature stream on modified carbon-containing electrodes for the 17-year period, the current review has been restricted on a method of analysis and analyte. So, the electrodes used for metal ion determination with SV have been described only. All the papers published over this period can be divided into six main groups depending on the type of the electrode used: glassy carbon (GCE), carbon paste (CPE), carbon-containing composite (CCE), impregnated graphite (IGE), thick-film graphite-containing (TFGE) electrodes, carbon microelectrodes (CME), and their arrays (ACME). As Fig. 1 suggests, GCE is the first with

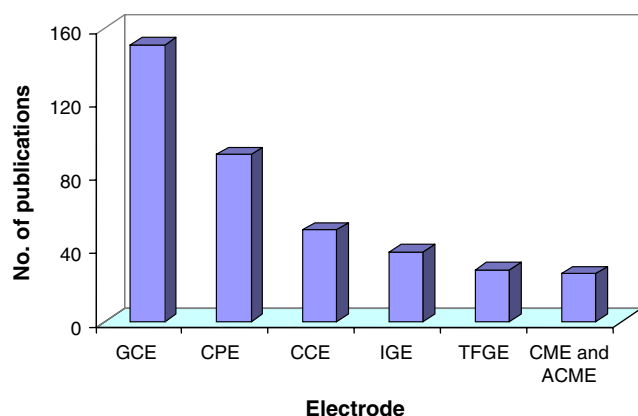
respect to the number of papers published over the 15 years. The minimum number of papers, most of which have appeared recently, are dedicated to TFGE and CME. This is due to the fact that these two groups of the electrodes represent recently emerging and vigorously developing lines of research into the use of carbon-containing electrodes.

### Glassy-carbon electrodes

Glassy carbon is isotropic, is almost gas-tight, has low porosity, is very hard, is a good current conductor, and is stable in many corrosive media [25]. The adsorptivity and the reactivity of glassy carbon are low compared to those of other structured graphite materials having a hexagonal or a rhombohedral lattice. These factors account for the low sensitivity of unmodified glassy-carbon electrodes in analysis [29–34]. The detection limit of elements is reduced by increasing the electrochemical accumulation time (up to 40 min) [35–42], using additional accumulation operations, e.g., the ultrasonic extraction [43] or modifying the GCE surface.

Table 1 shows some applications of modified GCE for voltammetric measurements of inorganic ions [44–190]. Methods of the preliminary modification of the surface (*ex situ*) and the *in-analysis* modification (*in situ*) are widely used for the purposeful transformation of the GCE surface properties. These methods are sometimes combined to enhance the selectivity. For example, a film of a metal or a current-conducting polymer is applied to GCE and a selective organic reagent or mercury, gold, or bismuth ions, which co-precipitate with the element to be determined, are added to the solution. GC is a preferable substrate for mercury film electrodes [191]. In this case, the two-layer modification of the surface is realized by the “*ex situ/in situ*” scheme. On occasion, up to three modified layers each, having its specific application and certain function, are built up on the surface. For example, the layer-by-layer modification by a clay mineral, a cation-exchange cross-linked polymer and mercury [156] results in that the GCE surface forms a layer, which possesses cation-exchange properties, can form an amalgam, and separates coarse molecules or cations.

The GCE modifiers in common use are metals (mercury [44–68], gold [81–85], cadmium [87], copper [88], lead [89], platinum [90], bismuth [91–96]) and facilitating the precipitation of amalgam-forming and electropositive elements. Organic substances (OS) [107–121], macrocyclic compounds [122–126], polymers [127–131, 157–159, 165–166, 169–175], bioactive compounds [186], and nanotubes [187–190] can also serve as GCE modifiers. Different combinations of the modifiers—a metal and OS [70–80, 97–105, 106], a polymer and a metal [86, 132–147, 160–



**Fig. 1** Representation of papers published in 1990–2005 depending on electrode type described

**Table 1** Modified glassy carbon electrodes

Modifier <sup>a</sup>	Manner	Analyte	Detection limit (M)	Supporting electrolyte <sup>b</sup>	Sweep mode <sup>c</sup>	Purge <sup>d</sup>	Sample <sup>e</sup>	Reference
Hg	In situ	Ni (II)	$2 \cdot 10^{-6}$	$30 \text{ gL}^{-1} \text{ H}_3\text{PO}_4 + 70 \text{ gL}^{-1} \text{ Na}_2\text{SO}_4 + 10 \text{ gL}^{-1} \text{ NaCl} + \text{Hg (II)} (\text{pH } 4.5)$	LS ASV	–	Nickel electrodeposits	[44]
Hg	In situ	Pd (II)	$9 \cdot 10^{-6}$	$0.2 \text{ M KCl} (\text{pH } 3) + \text{Hg (II)} (\text{Hg}:\text{Pd} \leq 1:10)$	LS ASV	–	BGD	[45]
Hg	In situ	Fe (II, III), Mn (II)	$1 \cdot 10^{-6}$	$0.5 \text{ M NaCl} + \text{Hg (II)} (\text{pH } 4.0-6.0 \text{ for Mn, pH } 3.5-4.0 \text{ for Fe})$	LS ASV	+	Sea, drinking, service waters	[46]
Hg	In situ	Pb (II), Cd (II)	$4.5 \cdot 10^{-12}$ (Cd); $1 \cdot 10^{-9}$ (Pb)	$0.01 \text{ M amm. buff. (pH } 5.6) + 5 \cdot 10^{-3} \text{ M SCN}^- + 3 \cdot 10^{-5} \text{ M Hg (II)}$	SQW ASV	+	Lake water	[47]
Hg	In situ	Cd (II), Pb (II), Cu (II)	$10^{-9}$	$0.1 \text{ M KNO}_3 + 0.03 \text{ M HNO}_3 + 1 \cdot 10^{-4} \text{ M Hg(NO}_3)_2$	LS ASV	–	BGD	[48]
Hg	In situ	Pb (II), Cd (II), Bi (III)	$5 \cdot 10^{-4}\%$ (Pb); $2 \cdot 10^{-5}\%$ (Cd); $7 \cdot 10^{-3}\%$ (Bi)	$0.35 \text{ M KCl} + 0.01 \text{ M HCl} + 5 \cdot 10^{-6} \text{ M Hg (II)} (\text{pH } 2.0)$	LS ASV	–	Soils, cement, rocks	[49]
Hg	In situ	Cu (II), Pb (II), Cd (II)	$10^{-9}-10^{-11}$	$1 \text{ M HClO}_4 + 5 \cdot 10^{-4} \text{ M Hg (II)}$	DP ASV	+	Sea waters	[50]
Hg	In situ	Cu (II), Pb (II), Cd (II)	$2 \cdot 10^{-5}$ (Pb); $7 \cdot 10^{-5}$ (Cd); $1.6 \cdot 10^{-4}$ (Cu)	$2 \text{ M NaCl} (0.5 \text{ M HCl}) + 1 \cdot 10^{-4} \text{ M Hg (II)}$	AC ASV	–	Surface, waste water	[51]
Hg	In situ	Pb (II), Cd (II), Cu (II), Zn (II)	$1 \cdot 10^{-9}$ (Pb); $1 \cdot 10^{-10}$ (Cd); $1 \cdot 10^{-8}$ (Cu); $1 \cdot 10^{-8}$ (Zn)	$1 \text{ M LiCl} (0.2 \text{ M HCl}) + 1 \cdot 10^{-4} \text{ M Hg(NO}_3)_2$	SQW ASV	+	Surface, waste water	[52–53]
Hg	In situ	Cu (II), Pb (II), Cd (II), Zn (II)	$2 \cdot 10^{-10}$ (Cu); $1 \cdot 10^{-10}$ (Pb); $7 \cdot 10^{-11}$ (Cd); $6 \cdot 10^{-10}$ (Zn)	$0.1 \text{ M NaAc} + 5 \cdot 10^{-5} \text{ M Hg (II)} (\text{Cu, Cd, Pb}); 0.1 \text{ M NaAc} + 5 \cdot 10^{-5} \text{ M Hg (II)} + \text{Ga (III)} (\text{Zn})$	LS ASV	–	Extract from river sediment	[54]
Hg	In situ	Cu (II), Pb (II), Cd (II), Zn (II)	$6 \cdot 10^{-11}$ (Zn); $2 \cdot 10^{-11}$ (Cd); $1 \cdot 10^{-11}$ (Pb); $5 \cdot 10^{-11}$ (Cu)	$0.025 \text{ M KCl} (\text{pH } 3.5) + 0.3 \text{ gL}^{-1} \text{ Hg (II)}$	DP ASV	+	Sea waters	[55]
Hg	Ex situ	Cu (II)	$2 \cdot 10^{-8}$	$0.1 \text{ M HNO}_3$	SQW ASV	–	Waters, pharmaceutical preparations	[56]
Hg	Ex situ	Pb (II)	$5 \cdot 10^{-9}$	$2.5 \text{ M NaCl} + 0.25 \text{ M asc. ac.} + 0.24 \text{ M NaOH}$	DP ASV	+	Soil, air	[57]
Hg	Ex situ	Tl (I)	$1 \cdot 10^{-9}$	$0.13 \text{ M EDTA} + 0.58 \text{ M asc. ac.} + 0.7 \text{ M NaOH}$	DP ASV	+	Soils	[58]
Hg	Ex situ	Tl (I)	$5 \cdot 10^{-10}$	$0.17 \text{ M EDTA} + 2 \text{ mM HCl} + 0.03 \text{ M asc. ac.}$	LS ASV	+	Natural waters	[59]

Table 1 (continued)

Modifier <sup>a</sup>	Manner	Analyte	Detection limit (M)	Supporting electrolyte <sup>b</sup>	Sweep mode <sup>c</sup>	Purge <sup>d</sup>	Sample <sup>e</sup>	Reference
Hg	Ex situ	Ba (II), Pb (II)	$7 \cdot 10^{-10}$ (Ba); $5 \cdot 10^{-10}$ (Pb);	0.1 M HClO <sub>4</sub> or 80% ethanol + 0.1 M TBAP	DP ASV	+	BGD	[60]
Hg	Ex situ	Pb (II), Cu (II)	$6 \cdot 10^{-11}$ (Pb); $2 \cdot 10^{-10}$ (Cu)	0.01 M NH <sub>4</sub> Ac–HCl + $1.2 \cdot 10^{-4}$ mM NaSCN (pH 3.4)	DP ASV	–	Sea water	[61]
Hg	Ex situ	Pb (II), Cu (II), Cd (II)	$10^{-9}$	0.05 M HCl + 70% methanol (pH 4–6)	DP ASV	+	Foodstuffs	[62]
Hg	Ex situ	Pb (II), Cu (II), Cd (II)	$10^{-7}$	0.1 M HNO <sub>3</sub> + 5–10 gL <sup>-1</sup> SDS	DP ASV	+	Fruit juice, wine, beer, milk powder, waste water	[63]
Hg	Ex situ	Zn (II), Cu (II), Pb (II), Cd (II)	$5 \cdot 10^{-10}$ – $1 \cdot 10^{-9}$	0.1 M KNO <sub>3</sub> + 2 mM HNO <sub>3</sub>	SQW ASV	–	Waste water	[64]
Hg	Ex situ	Zn (II), Cu (II), Pb (II), Cd (II)	$4 \cdot 10^{-7}$ (Zn); $2.7 \cdot 10^{-9}$ (Cd); $6.8 \cdot 10^{-9}$ (Pb); $4 \cdot 10^{-8}$ (Cu)	0.2 M HNO <sub>3</sub>	SQW ASV	–	Sweet water	[65]
Hg	Ex situ	Zn (II), Cu (II), Pb (II), Cd (II)	$8 \cdot 10^{-9}$ (Zn); $9.7 \cdot 10^{-9}$ (Cu); $1.6 \cdot 10^{-8}$ (Pb); $8.6 \cdot 10^{-9}$ (Cd)	0.01 M LiCl (pH 2.9)	SQW ASV	+	Fuel	[66]
Hg	Ex situ	Cu (II), Pb (II), Cd (II)	$1 \text{ ng g}^{-1}$	0.075 M NaNO <sub>3</sub>	LS ASV	+	Sugar, syrup	[67]
Hg	Ex situ	Cu (II), Pb (II), Cd (II), Zn (II)	$10^{-8}$ – $10^{-9}$	0.1 M citric acid + $1 \cdot 10^{-4}$ M Fe (III)	LS ASV	–	BGD, extracts from turf	[68]
Hg/Cu	Ex situ/ in situ	Se (IV), Zn (II)	$1 \cdot 10^{-9}$	0.1 M HClO <sub>4</sub> + 1 mgL <sup>-1</sup> Cu (II) + 0.02 M NaSCN + $5 \cdot 10^{-3}$ M EDTA	DP CSV	+	BGD	[69]
Hg, 8HXQ	In situ	Mo (VI)	$5 \cdot 10^{-9}$	0.2 M NaAc (pH 5.25) + $5 \cdot 10^{-5}$ M Hg (II) + $10^{-3}$ M 8HXQ	DP CSV	+	Biomaterials and background objects	[70]
Hg, DMG	In situ	Ni (II)	$1.3 \cdot 10^{-10}$	0.1 M KNO <sub>3</sub> + $2 \cdot 10^{-4}$ M DMG + $5 \cdot 10^{-5}$ M Hg(NO <sub>3</sub> ) <sub>2</sub> (pH 9)	SQW CSV	–	Soils	[71]
Hg/RSH	Ex situ	Cd (II)	$4 \cdot 10^{-12}$	0.01 M NaAc (pH 3.0)	SQW CSV	+	Sea water	[72]
Hg, catechol	In situ	Sn (IV), Pb (II)	$5 \cdot 10^{-9}$ (Pb); $4 \cdot 10^{-9}$ (Sn)	0.1 M NaAc (pH 4.5) + $5 \cdot 10^{-4}$ M catechol + 1 gL <sup>-1</sup> Hg (II)	DP CSV	+	Biomaterials, foodstuffs, background objects	[73–74]

Hg/ EDA	Ex situ/ in situ	Cu (II)		0.01 M HCl + $3 \cdot 10^{-3}$ M EDA	SQW ASV	–	Sea water	[75]
Hg/ DMG	Ex situ/ in situ	Ni (II)	$10^{-6}$	0.25 M $\text{NH}_3$ + 0.25 M $\text{NH}_4\text{NO}_3$ + 0.25 M NaSCN + $1 \cdot 10^{-4}$ M DMG	LS CSV	–	BGD	[76]
Hg/18C6	Ex situ/ in situ	Pb (II)	$1 \cdot 10^{-4}$	0.1 M $\text{LiNO}_3$ (or $\text{LiClO}_4$ ) + $2.9 \cdot 10^{-3}$ M 18C6	SQW ASV	+	BGD	[77]
Hg/ CHD or DMG	Ex situ/ in situ	Co (II), Ni (II)	$1 \cdot 10^{-9}$	30 mM HEPES + 0.1 M $\text{NaClO}_4$ (pH 7.4) + CHD or DMG	DP CSV	+	Model mixtures	[78]
Hg/ CHD or DMG	Ex situ/ in situ	Co (II), Ni (II)	$5 \cdot 10^{-9}$ (Ni); $2 \cdot 10^{-9}$ (Co)	0.1 M HEPES (pH 7.4) + $1 \cdot 10^{-4}$ M CHD or DMG	SQW CSV	–	Biological liquids	[79]
Hg/ DMG (1), Hg/ 8HXQ (2)	Ex situ/ in situ	Ni (II) (1), Cu (II) (2)	$9 \cdot 10^{-10}$ (Ni), $1 \cdot 10^{-9}$ (Cu)	0.1 M amm. buff. (pH 9) + 0.001 M DMG (Ni); 0.01 M PIPES (pH 6.8) + $5 \cdot 10^{-5}$ M 8HXQ (Cu)	SQW CSV	–	BGD	[80]
Au	Ex situ	As (III)	$1.6 \cdot 10^{-8}$	HCl + $\text{Na}_2\text{SO}_3$	DP ASV	+	Natural waters	[81]
Au nanoparticles	Ex situ	As (III)	$1.3 \cdot 10^{-10}$ (LS ASV); $2 \cdot 10^{-10}$ (SQW ASV)	1 M HCl	LS ASV SQW ASV	+	River waters	[82]
Au	Ex situ	Au (III)	$4 \cdot 10^{-9}$	0.7 M HCl + 0.32 M $\text{HNO}_3$	DP ASV	–	SS of gold ore	[83]
Au	Ex situ	$\text{CH}_3\text{Hg}^+$	$2 \cdot 10^{-8}$	0.1M $\text{NaNO}_3$ + 0.14 M $\text{HNO}_3$	DP ASV	–	Model solution	[84]
Au	Ex situ	Se (IV), Te (IV)	$1.3 \cdot 10^{-10}$ (Se); $1.6 \cdot 10^{-10}$ (Te)	0.1 M $\text{HNO}_3$	DP ASV	+	Copper	[85]
Au/PVP	Ex situ	Hg (II)	$5 \cdot 10^{-10}$	0.025 M $\text{H}_2\text{SO}_4$ + 0.05 M KCl	SQW ASV	–	Natural waters	[86]
Cd	In situ	Hg (II)	$4.5 \cdot 10^{-9}$	0.1 M $\text{NH}_4\text{Br}$ + $10^{-8}$ M Cd (II)	LS ASV	–	Natural waters	[87]
Cu (1); Au (2); Se (3)	In situ	Se (IV), Au (III)	$3.8 \cdot 10^{-5}$ (Se), $1.5 \cdot 10^{-5}$ (Au)	0.1 M $\text{HClO}_4$ + $16(10)$ $\text{mgL}^{-1}$ Cu(II) (Au(III)) (Se); 0.1 M $\text{HClO}_4$ + $10 \text{ mgL}^{-1}$ Se (IV) (Au)	SQW CSV	–	Vitamins	[88]
Pb	In situ	Ni (II), Co (II)	$1.6 \cdot 10^{-9}$ (Ni); $1 \cdot 10^{-9}$ (Co)	0.1 M PIPES + $5 \cdot 10^{-3}$ M DMG + $2.5 \cdot 10^{-5}$ M $\text{Pb}(\text{NO}_3)_2$ (pH 6–9)	SQW CSV	–	SS of water and tea leaves	[89]
Pt nanoparticles	In situ	As (III)	$2.8 \cdot 10^{-8}$	1 M $\text{HClO}_4$	LS ASV	+	Drinking water	[90]
Bi	In situ	In (III)	$10^{-8}$	0.1 M NaAc (pH 4.5) + 0.1 M KBr + $200 \text{ } \mu\text{gL}^{-1}$ Bi (III)	SQW ASV	–	Model solutions	[91]
Bi	In situ	Zn (II), Cd (II), Pb (II)	$1 \cdot 10^{-9}$ (Pb); $2 \cdot 10^{-9}$ (Cd); $1 \cdot 10^{-8}$ (Zn)	0.1 M NaAc + $500 \text{ } \mu\text{gL}^{-1}$ Bi (III)	SQW ASV	–	Tap water, biomaterials	[92]
Bi	Ex situ	Cu (II)	$7.8 \cdot 10^{-8}$	0.1 M acet. buff. (pH 4.75) + $2.5 \cdot 10^{-4}$ M Ga (III)	SQW ASV		Model solution	[93]
Bi	Ex situ	Cd (II), Pb (II)	$5 \cdot 10^{-7}$	0.05 M NaAc	SQW ASV	–	BGD	[94]
Bi	Ex situ	Zn (II), Cd (II)	$4.3 \cdot 10^{-7}$ (Zn); $5.9 \cdot 10^{-9}$ (Cd)	0.1 M NaAc	SQW ASV	–	BGD	[95]
Bi	Ex situ	In (III), Tl (I), Cu (II), Cd (II)	$10^{-7}$	0.1 M NaAc (pH 4.5)	SQW ASV	–	BGD	[96]

Table 1 (continued)

Modifier <sup>a</sup>	Manner	Analyte	Detection limit (M)	Supporting electrolyte <sup>b</sup>	Sweep mode <sup>c</sup>	Purge <sup>d</sup>	Sample <sup>e</sup>	Reference
Bi/ CAA	Ex situ/ in situ	Pb (II), Zn (II) V (V)	2·10 <sup>-8</sup>	0.1 M acet. buff. (pH 5.5) + 50 μM CAA + 4 mM KBrO <sub>4</sub>	SQW CSV	–	Groundwater	[97]
Bi/ DMG	Ex situ/ in situ	Co (II)	1.8·10 <sup>-11</sup>	0.0125 M PIPES + 0.002 M HEPES + 75 mgL <sup>-1</sup> CTAB + 2.4·10 <sup>-4</sup> M DMG (pH 6.5)	DP CSV	+	Tea leaves, natural and drinking waters	[98–99]
Bi/ CF	Ex situ/ in situ	Cr (VI)	2·10 <sup>-9</sup>	0.01 M PIPES + 0.2 M KCl + 0.1 mM CF	SQW CSV	–	Tap water, soils	[100]
Bi/TEA	Ex situ/ in situ	Fe (III)	7.7·10 <sup>-9</sup>	0.1 M NaOH + 0.01 M TEA + 5·10 <sup>-3</sup> M KBrO <sub>3</sub>	DP CSV	+	Standard sample of river water	[101]
Bi/ DTPA	Ex situ/ in situ	Cr (VI)	3·10 <sup>-10</sup>	0.1 M NaAc (pH 4.5) + 0.25 M KNO <sub>3</sub> + 1·10 <sup>-6</sup> M DTPA	SQW CSV	+	River waters	[102]
Bi/ DMG	Ex situ/ in situ	Co (II), Ni (II)	1.2·10 <sup>-9</sup> (Co); 1.7·10 <sup>-9</sup> (Ni)	0.2 M amm. buff. (pH 9.2) + 1·10 <sup>-4</sup> M DMG	SQW ASV	–	Ore, river water	[103]
Bi/ CAA	Ex situ/ in situ	Mo (VI)	2·10 <sup>-9</sup>	0.05 M acet. buff. (pH 5.5) + 5·10 <sup>-5</sup> M CAA	SQW CSV	–	Sea water	[104]
Bi/cupferron	Ex situ/ in situ	U (VI)	4·10 <sup>-10</sup>	0.01 M PIPES + 0.05 M KCl + 0.1 mM cupferron	SQW CSV	–	Sea water	[105]
Pb-Cu/DMG + NO <sub>2</sub> <sup>-</sup>	In situ	Co (II)	1·10 <sup>-11</sup>	0.2 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + NH <sub>4</sub> OH + 0.5 M NaNO <sub>2</sub> + 2·10 <sup>-3</sup> M DMG + 5·10 <sup>-5</sup> M Cu (II) + 1.5·10 <sup>-5</sup> M Pb (II) (pH 8.5)	SQW CSV	–	SS, water	[106]
8HXQ	In situ	Sn (II)	2·10 <sup>-6</sup>	0.1 M NaAc (pH 6) + 8HXQ	SQW	+	Tooth paste, pharmaceutical preparations	[107]
HEPES	In situ	U (VI)	1·10 <sup>-9</sup>	0.02 M HClO <sub>4</sub> (pH 4) + 2·10 <sup>-5</sup> M HEPES	SQW CSV	+	Food stuffs, fertilizers, cement	[108]
TMAC	In situ	Al (III), Mg (II)	5·10 <sup>-11</sup> (Al); 4·10 <sup>-10</sup> (Mg)	0.01 M KNO <sub>3</sub> (pH 5.0) + 0.02 M TMAC	SQW ASV	+	Food stuffs, fertilizers, cement	[109]
DFO	In situ	Al (III)	2·10 <sup>-7</sup>	0.05 M amm. buff. (pH 8.3–8.9) + (10 <sup>-4</sup> –10 <sup>-5</sup> ) M DFO, THMP, DHP	DP ASV	–	Natural waters, biological liquids	[110]
DDTACD	Ex situ	Au (III)	8.3·10 <sup>-8</sup>	0.1 M NaCl + 0.01 M NaAc (pH 4)	SQW CSV	–	Geological samples	[111]
8MQN	Ex situ	Ag (I)	2.7·10 <sup>-11</sup>	0.1 M NaAc (pH 4.3) (accumulation), 0.1 M HNO <sub>3</sub> + 0.05 M KBr (sweep)	LS ASV	–	Sea waters, rice	[112]
PAN	Ex situ	Cd (II)	5·10 <sup>-10</sup>	0.1 M NaH <sub>2</sub> PO <sub>4</sub>	LS ASV	–	Model solution	[113]
ARS	In situ	Cu (II)	1·10 <sup>-6</sup>	0.1 M H <sub>3</sub> PO <sub>4</sub> + 0.1 M ARS	CV	–	BGD	[114]
Alizarin	Ex situ	Cu (II)	1·10 <sup>-4</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub> (pH 4)	CV	–	BGD	[115]
BPD	In situ	Fe (II)	10 <sup>-7</sup>	0.025 M KCl + 1 gL <sup>-1</sup> BPD	DP AVA	+	Soils	[116]
Dithizone	Ex situ	Hg (II)	5·10 <sup>-10</sup>	0.1 M KJ (pH 2)	LS ASV	–	Sea water	[117]
MAA	Ex situ	Hg (II)	4·10 <sup>-2</sup>	0.1 M HNO <sub>3</sub>	LS ASV	–	BGD	[118]
BPD	Ex situ	Pb (II)	1·10 <sup>-7</sup>	0.1 M NaAc (pH 4.5)	LS ASV	+	Model solutions	[119]

Humic acids	Ex situ	Fe (II), Cu (II), Ni (II)	$2.0 \cdot 10^{-6}$ (Fe); $6.0 \cdot 10^{-7}$ (Cu); $6.0 \cdot 10^{-6}$ (Ni)	0.1 M KHPH (Fe, Cu); 0.1 M Na <sub>2</sub> SO <sub>4</sub> (Ni)	SQW ASV	–	BGD	[120]
PCC	Ex situ	Ce (III)	$2.0 \cdot 10^{-10}$	0.1 M NaOH	DP ASV	+	SS, hair	[121]
KF-222	Ex situ	Hg (II)	$10^{-12}$	0.01 M NaAc (pH 4) + 0.1 M NaClO <sub>4</sub>	SQW ASV	–	Sea and waste waters, saliva	[122– 123]
CA	Ex situ	Hg (II)	$2.5 \cdot 10^{-8}$	0.1 M H <sub>2</sub> SO <sub>4</sub> + 0.01 M NaCl	SQW ASV	+	Natural waters	[124]
TCA	Ex situ	Cu (II)	$2 \cdot 10^{-9}$	0.1 M B-R (pH 4.5)	DP ASV	+	Natural waters	[125]
TCA	Ex situ	Pb (II), Cd (II)	$2 \cdot 10^{-8}$ (Cd); $8 \cdot 10^{-9}$ (Pb)	0.1 M acet. buff.	DP ASV	+	Natural waters	[126]
Nafion	Ex situ	Pb (II)	$5 \cdot 10^{-9}$	0.1 M NaCl + 0.05 M HCl	SQW ASV	–	Standard sample TMDA- 52.2	[127]
Nafion	Ex situ	Sn (IV)	$8 \cdot 10^{-10}$	0.01 M NaCl + HCl (pH 1.9)	LS CSV	–	Hair	[128]
Nafion	Ex situ	CH <sub>3</sub> Hg <sup>+</sup>	$4.5 \cdot 10^{-8}$	0.01 M HClO <sub>4</sub>	SQW AV	+	BGD	[129]
Nafion	Ex situ	Fe (III), Fe (II)	$10^{-9}$	(0.03–0.3) M HCl	SQW DDV	+	Interstitial waters	[130– 131]
Nafion /Hg	Ex situ	Cd (II)	$1 \cdot 10^{-10}$	0.01 M NaAc	LS ASV	+	Blood	[132]
Nafion /Hg	Ex situ	Cu (II)	$1.6 \cdot 10^{-6}$	0.1 M HNO <sub>3</sub>	SQW ASV	+	Beer	[133]
Nafion /Hg	Ex situ	Cu (II)	$1.5 \cdot 10^{-8}$	0.1 M acet. buff. (pH 3.5)	DP ASV	+	Estuarial water	[134]
Nafion /Hg	Ex situ	Pb (II)	$2 \cdot 10^{-7}$	0.1 M TRIS + 0.6 M NaCl	SQW ASV	+	BGD	[135]
Nafion /Hg	Ex situ	Pb (II)	$1 \cdot 10^{-7}$	0.02 M KNO <sub>3</sub> (pH 5)	DP ASV	+	Model solution	[136]
Nafion /Hg	Ex situ/ in situ	Pb (II)	$1.2 \cdot 10^{-9}$	0.1 M NaAc (pH 4.6) + 85.7 mM Hg (II)	SQW ASV	–	Simulated saliva	[137]
Nafion /Hg	Ex situ/ in situ	Cd (II), Pb (II)	$2 \cdot 10^{-9}$ M (Cd); $4 \cdot 10^{-9}$ M (Pb)	0.1 M KNO <sub>3</sub> + 2 mM HNO <sub>3</sub> + $1 \cdot 10^{-4}$ M Hg (II)	SQW ASV	–	Waste water	[138]
Nafion /Hg	Ex situ	Pb (II), Cd (II)	$3 \cdot 10^{-11}$ (Pb), $5 \cdot 10^{-11}$ (Cd)	0.1 M NaAc (pH 4.6)	SQW ASV	–	BGD	[139– 140]
Nafion /Hg	Ex situ	Pb (II), Cd (II)	$9 \cdot 10^{-9}$ (Cd), $1 \cdot 10^{-7}$ (Pb)	0.12 M NaAc (pH 7.7)	SQW ASV	+	Sweet water	[141]
Nafion /Hg	Ex situ	Pb (II), Cu (II)	$2 \cdot 10^{-8}$ (Pb), $6 \cdot 10^{-8}$ (Cu)	0.1 M KNO <sub>3</sub> + 5 mM HNO <sub>3</sub>	DP ASV	–	Service waters	[142]
Nafion /Hg	Ex situ	Cd (II), Pb (II)	$4.5 \cdot 10^{-8}$ (Cd); $4.8 \cdot 10^{-8}$ (Pb)	0.1 M NaAc (pH 4.5) + $9.41 \cdot 10^{-5}$ M FA	DP ASV SQW ASV	+	Model solutions of fulvic acids	[143]
Nafion /Hg	Ex situ	Cu (II), Pb (II), Cd (II)	$1.6 \cdot 10^{-8}$ (Cu); $4.8 \cdot 10^{-9}$ (Pb); $8.9 \cdot 10^{-9}$ (Cd)	0.1 M NaAc (pH 4.5)	DP ASV, LS CSV	+	Food stuffs	[144]
Nafion / Hg–Cu	Ex situ	Pb (II)	$4 \cdot 10^{-10}$	5 mM HNO <sub>3</sub> + 0.1 M KNO <sub>3</sub>	SQW ASV	+	Natural waters	[145]
Nafion /Bi	Ex situ/ in situ	Pb (II), Cd (II)	$4.8 \cdot 10^{-8}$	0.1 M NaAc (pH 4.5) + 400 µg L <sup>-1</sup> Bi (III)	SQW ASV	–	Model solutions of SAS	[146]
Nafion /Bi	Ex situ/ in situ or ex situ	Pb (II), Cd (II), Zn (II)	$5 \cdot 10^{-10}$ (Pb); $9 \cdot 10^{-10}$ (Cd); $6 \cdot 10^{-9}$ (Zn)	0.1 M acet. buff.	SQW ASV	–	Tap water, urine, wine	[147]

**Table 1** (continued)

Modifier <sup>a</sup>	Manner	Analyte	Detection limit (M)	Supporting electrolyte <sup>b</sup>	Sweep mode <sup>c</sup>	Purge <sup>d</sup>	Sample <sup>e</sup>	Reference
Nafion + HgCl <sub>2</sub>	Ex situ	Pb (II), Cu (II)	5.8·10 <sup>-9</sup> (Pb); 5·10 <sup>-8</sup> (Cu)	0.1 M citric acid + 0.03 M Na <sub>2</sub> HPO <sub>4</sub> + 0.1 M KCl	LS ASV	–	Sea water	[148]
Nafion + KF-222 (1); Nafion + terpene (2)	Ex situ	Hg (II)	3.8·10 <sup>-9</sup> (Hg); 2.5·10 <sup>-7</sup> Fe (II)	0.025 M H <sub>2</sub> SO <sub>4</sub> + 0.1 M NaCl (Hg); 0.1 M sulphate buffer (pH 3) (Fe)	SQW ASV SQW CSV	–	BGD	[149]
Nafion + Na-DDC (1); Nafion + 18C6 (2)	Ex situ	Fe (II) (2) Pb (II), Cu (II), Cd (II), Hg (II)	1·10 <sup>-8</sup> (Hg) (1), 1·10 <sup>-9</sup> (Cu, Pb, Cd) (2),	0.1 M KNO <sub>3</sub> (pH 2.0) (1); 0.1 M NaAc (2)	DP ASV	+	BGD	[150]
Nafion + tobramycin	Ex situ	Cu (II)	5·10 <sup>-10</sup>	Acet. buff. (pH 4.6)	DP ASV	–	Water samples, analytical salts	[151]
Nafion + BPD/Hg	Ex situ	Pb (II)	5·10 <sup>-10</sup>	0.07 M phosphate buffer (pH 4)	SQW ASV	–	Drinking water	[152]
Nafion + DAB/Hg	Ex situ	Se (IV)	6·10 <sup>-9</sup>	0.1 M NaClO <sub>4</sub>	SQW CSV	–	Natural waters	[153]
Nafion + 8HXQ/Hg	Ex situ	Te (IV)	1.6·10 <sup>-9</sup>	0.1 M NaClO <sub>4</sub> (pH 2.5) + 0.01 M EDTA	SQW CSV	+	BGD	[154]
Nafion + DMG; BPD/ Hg	Ex situ	Pb (II), Cu (II)	6.3·10 <sup>-8</sup> (Cu); 1·10 <sup>-8</sup> (Pb)	NH <sub>3</sub> /NH <sub>4</sub> Cl buffer (pH 9)	SQW ASV	–	Waters, urine	[155]
Nontronite /nafion/Hg	Ex situ	Cu (II)	10 <sup>-7</sup>	0.01 M KNO <sub>3</sub>	SQW ASV	+	Natural waters	[156]
Tosflex	Ex situ	Cu (II)	9.4·10 <sup>-6</sup>	0.5 M NaCl + 0.1 M NaAc (pH 5)	LS ASV	+	BGD	[157]
Tosflex	Ex situ	Hg (II)	2·10 <sup>-11</sup>	0.5 M NaCl + 0.01 M HCl	DP ASV	+	Natural waters	[158– 159]
Tosflex/Hg	Ex situ	Bi (III)	3·10 <sup>-9</sup>	0.5 M KCl (pH 1.4)	SQW ASV	+	Waters	[160]
Tosflex/Hg	Ex situ	Tl (III)	5·10 <sup>-10</sup>	0.5 M KCl (pH 5.6)	SQW ASV	–	Model solutions	[161]
Tosflex/Hg	Ex situ	Zn (II)	1.5·10 <sup>-9</sup>	0.02 M H <sub>2</sub> SO <sub>4</sub>	SQW ASV	+	Model solutions	[162]
Tosflex + DAB/Hg	Ex situ	Se (IV)	1.3·10 <sup>-9</sup>	0.1 M KCl	SQW CSV	+	Sea and sweet natural waters	[163]
Tosflex + 8HXQ/Hg	Ex situ	Te (IV)	1.6·10 <sup>-9</sup>	0.1 M KCl (pH 3)	SQW CSV	+	Model solutions	[164]
PPG	Ex situ	Sb (III)	4.1·10 <sup>-10</sup>	0.04 M NaAc (pH 5.5) (accumulation); 1.0 M HCl (sweep)	DP ASV	+	Sea water, hair	[165]
PPD	Ex situ	Hg (II)	1·10 <sup>-10</sup>	0.5 M NaCl + 0.01 M HCl	DP ASV	+	Interstitial waters	[166]
PP + PDDT	Ex situ	Cu (II)	1·10 <sup>-6</sup>	0.1 M NaAc	CV	–	Model solution	[167]
PMR	Ex situ	Hg (II)	4.4·10 <sup>-11</sup>	B-R buff. (pH 2.56)	LS ASV	–	Like water	[168]
CA	Ex situ	Pb (II), Cd (II)	2·10 <sup>-7</sup>	0.1 M NaAc	DP ASV	+	Model solution	[169– 170]
Nontronite/CA	Ex situ	Cu (II)	2.7·10 <sup>-8</sup>	amm. buff. (pH 10)	SQW ASV	–	Natural waters	[171]
OxPPH or Morin hydrate	Ex situ	Sn (II, IV), Sb (III)	5·10 <sup>-8</sup> (Sn); 5·10 <sup>-8</sup> (Sb)	0.5 M HCl + 1.5 M NaCl	LS ASV	–	Natural waters	[172– 173]



polymer – EDTA	Ex situ	Pb (II), Cu (II), Hg (II)	$6 \cdot 10^{-10}$ (Pb); $2 \cdot 10^{-10}$ (Cu); $5 \cdot 10^{-10}$ (Hg)	0.2 M NaAc	SQW ASV +	Tap water, SS of river	[174]
PDDT – EDTA	Ex situ	Ni (II), Zn (II), Cd (II), Hg (II), Cu (II), Pb (II), Co (II), Fe (II)	$6.0 \cdot 10^{-8}$ (Ni); $9.0 \cdot 10^{-8}$ (Zn); $6.6 \cdot 10^{-8}$ (Cd); $0.3 \cdot 10^{-9}$ (Hg); $0.1 \cdot 10^{-9}$ (Cu); $0.4 \cdot 10^{-9}$ (Pb); $5.0 \cdot 10^{-8}$ (Co); $8.0 \cdot 10^{-8}$ (Fe)	0.2 M NaAc (pH 2.1; 2.5; 3.0; 4.1; 4.5; 4.9; 5.3; 5.7 for Ni, Zn, Cd, Hg, Cu, Pb, Co, Fe)	SQW ASV –	BGD	[175]
PVP + KF222	Ex situ	Hg (II)	$1 \cdot 10^{-9}$	0.025 M H <sub>2</sub> SO <sub>4</sub> + 0.1 M NaCl	DP ASV –	BGD	[176]
PVP /Hg	Ex situ	Pb (II)	$1.5 \cdot 10^{-9}$	0.025 M H <sub>2</sub> SO <sub>4</sub>	SQW ASV –	Subsoil waters	[177]
PVP /Hg	Ex situ	Tl (III)	$5 \cdot 10^{-10}$	0.01 M HNO <sub>3</sub> + 0.1 M KCl	SQW ASV –	Subsoil waters	[178]
CA/Hg	Ex situ	Pb (II)	$1.9 \cdot 10^{-7}$	0.1 M NaAc (pH 4.6)	DP ASV +	Model solutions	[179]
PP /Hg	Ex situ	Cd (II), Pb (II)	$1 \cdot 10^{-6}$	0.1 M NaAc	SQW ASV +	BGD	[180]
PESA /Hg	Ex situ/ in situ	Cd (II), Pb (II)	$3.7 \cdot 10^{-9}$ (Cd); $3.8 \cdot 10^{-9}$ (Pb)	0.1 M KNO <sub>3</sub> + 5 mM HNO <sub>3</sub> + 0.1 mM Hg (II)	SQW ASV –	Model solutions of SAS	[181]
PSSF /Hg; Hg /PLL-PSS	Ex situ	Pb (II), Cd (II), Cu (II)	$1.2 \cdot 10^{-10}$ (Pb); $9 \cdot 10^{-10}$ (Cu); $6.5 \cdot 10^{-10}$ (Cd)	0.5 M NaCl	SQW ASV –	Natural waters	[182– 184]
PSSF + chabazite /Hg	Ex situ	Zn (II)	$5 \cdot 10^{-7}$	0.01 M KNO <sub>3</sub>	SQW ASV +	Model solutions	[185]
leaven	In situ	Au (III)	$6.0 \cdot 10^{-8}$	0.1 M HCl + 0.1 M HNO <sub>3</sub>	LS CSV +	BGD	[186]
CNT	Ex situ	Hg (II)	$2 \cdot 10^{-10}$	0.1 M HCl + 0.02 M KJ	DP ASV –	Lake water	[187]
CNT	Ex situ	Cd (II), Pb (II)	$6 \cdot 10^{-9}$ (Cd); $4 \cdot 10^{-9}$ (Pb)	0.1 M NaAc + 0.02 M KJ	DP ASV –	Lake water	[188]
CNT + Nafion	Ex situ	Cd (II)	$4 \cdot 10^{-9}$	Acet. buff. (pH 5)	DP ASV –	Water samples	[189]
GCM-Au/MWCNT	Ex situ	Tl (I)	$2 \cdot 10^{-6}$	10 mM HNO <sub>3</sub> + 10 mM NaCl	LS ASV –	BGD	[190]

<sup>a</sup> CAA Chloranilic acid, *SHXQ* 8-hydroxyquinoline, *DMG* dimethylglyoxime, *RSH* ω-mercaptopcarboxylic acid, *EDA* ethylenediamine, *18C6* 18-crown-6-ether, *CHD* 1,2-cyclohexanedione dioxime, *PVP* poly(4-vinylpyridine), *CAA* chloranilic acid, *CF* cupferron, *TEA* triethanolamine, *DTPA* diethylene triamine pentaacetic acid, *TMAAC* tetramethylammonium chloride, *DFO* diferrinoxamine, *DDTACD* 8,9,17,18-dibenzo-1,7-dioxo-10,13,16-triazacyclocloctadecane, *8MQN* 8-mercaptopquinoline, *PAN* polyacrylonitrile, *ARS* alizarin red S, *BPD* 2,2'-bipyridyl, *PCC* pyrocatechol, *KF-222* Cryptofix-222, *MAA* mercaptoacetic acid, *CA* calix[6]arene, *TCA* *p-tert*-butylthiacalix[4]arene, *PES* poly(estersulfonate), *DDC* diethyldithiocarbamate (e.g., Na, Zn), *DAB* 3,3'-diaminobenzidine, *PPG* polypyrrolol, *HEPES* *N*-(2-hydroxyethyl)piperazine-*N'*-3-propane sulfonic acid, *PPD* PP derivative, *PP* polypyrrole, *PDDT* (pyridyl)-5,6-diphenyl-4,4'-disulfonate-1,2,4-triazine, *PMR* polymethyl-red, *CA* cellulose acetate, *OxPPh* oxidized polyphenol, *EDTA* ethylenediaminetetraacetic acid, *PDIT* poly-3',4'-diamino-2,2',5',2''-terthiophen, *PESA* poly(ester sulfonic) acid, *PSSF* poly(styrene sulfonate), *PLL-PSS* poly-L-lysine-poly(sodium 4-styrenesulfonate), *CNT* carbon nanotubes

<sup>b</sup> *Ammonium* buffer, *asc.ac.* ascorbic acid, *TBAP* tetrabutylammonium perchlorate, *SDS* sodium dodecyl sulfate, *PIPES* piperazine-*N,N'*-bis(2-ethane sulfonic acid), *CTAB* cetyl trimethylammonium bromide, *THMP* 3-hydroxy-2-methyl-4H-pyran-4-one, *DHP* 2,3-dihydroxypyridine, *KHPh* potassium hydrophthalate, *acet.buff.* acetate buffer, *TRIS* tris(hydroxymethyl) methylamine, *FA* fulvic acids, *TEA-Br* tetraethylammonium bromide, *B-R buff.* Britton-Robinson buffer

<sup>c</sup> *LS* Linear sweep, *ASV* anodic stripping voltammetry, *SQW* square wave, *DP* differential pulse, *AC* alternating current, *CSV* cathodic stripping voltammetry, *CV* cyclic voltammetry, *AlVA* anodic voltammetry, *DDV* double differential voltammetry, *MSWV* multiple square wave voltammetry

<sup>d</sup> + After, – without oxygen removal

<sup>e</sup> *BGD* Supporting electrolyte, *SS* standard sample, *SAS* surface active substances

162, 177–184], a polymer and OS [149–151, 167, 174–176], a polymer, OS, and a metal [152–155, 163–164, 185]—are used for the GCE surface modification. Water-soluble OS are generally immobilized in situ onto the surface of a pre-activated electrode [70–71, 73–80, 97–110, 114, 116], while low-soluble OS are immobilized ex situ [72, 111–113, 115, 117–126, 149–155, 185]. OS are localized on either the GCE surface [107–126] or the first modifying layer of mercury [70–80], bismuth [97–105] or lead–copper [106].

For a more profound immobilization of the compounds, GCE is pre-polarized at a constant potential of (1.2±2.0) V [36, 39, 41] or undergoes multiple (up to 100) polarization cycles between 0 and +1.2 V in 0.1 M NaOH [40]. Some investigators think that, in this case, new functional groups appear on the surface [39–41], whereas others are inclined to consider the formation of an oxidized GC film [36]. Still, they are agreed that the anodic polarization radically changes the structure and the composition of the electrode surface, making it possible to fix the modifier or the measured ions on the surface through the ion exchange, the covalent bonding or the electrostatic interaction.

Polymer-coated electrodes constitute a big group of GCE [127–183]. Unique properties of the polymer surface and applications of current-conducting polymers are described in Ivaska [192]. To make a polymer film in the form of a “spin coat”, several droplets of the liquid polymer are placed in the working zone, and the electrode is spindled until the polymer film is uniform in thickness. One more method for making of a polymer film (polyaniline, polypyrogallol, polycatechol, etc.) consists in its oxidative electro-polymerization growing from a monomer solution. It was proposed to make superfine (3,000 Å) polymer films on GCE by an original method of “electrostatic spraying” [169, 170], which involves preparation of a “spray liquid” under the action of a strong electric field. For example, to apply a cellulose acetate film, a strong electric field (the voltage of 14 kV) was applied to a dielectric mixture, which was composed of cellulose acetate, acetone, and magnesium perchlorate (a porophore). The liquid was charged and was broken into tiny droplets so that a thin, uniform, and homogeneous film covered the electrode. The polymer electrode films generally have a cross-linked structure and act as molecular sieves separating coarse particles, e.g., protein molecules. Moreover, they can function as ion exchangers. For example, nafion and tosflex (fluocarbon polymers) act as a cation exchanger and an anion exchanger, respectively. Some investigators implanted analytical reagents into the structure of current-conducting polymers [148–154, 162–163, 178] providing the enhanced selectivity of the polymer film. The high selectivity to metal ions was achieved [174–175] because polymers with covalently grafted ethylenediaminetetraacetic acid (EDTA)

groups were synthesized on GCE. The response selectivity is efficiently improved by the “guest–host” interaction. Properties of crown ethers acting as host molecules for ions of guest metals were used [77, 112, 108–109, 148–149, 176] for measurements of Au (III), Hg (II), Cu (II), Pb (II), and Cd (II) ions on electrodes modified by crown-ether adsorption and a nafion film with immobilized macrocycles.

One more method for improvement of the voltammetric selectivity is the use of electrodes with monolayers of organic molecules self-organized on the electrode surface [72, 193–194]. For example,  $\omega$ -carboxylic acids with hydrocarbon chains of different lengths can arrange themselves to the Langmuir palisade on gold or mercury surfaces. While possessing discrimination properties, functionalized layers can change the transport of depolarizer particles to the electrode surface not only due to different charges, but also due to the hydrophobic effect.

The pioneering studies concerned with the use of nanotube-modified GCE include the research performed by a group of Taiwan investigators [187, 188]. Such electrodes provided sufficiently low detection limits for elements. However, the introduction of these electrodes to the analytical practice requires solving the problem of structural ordering in the nanotube layer which influences the reproducibility of measurement results.

A serious problem in the use of GCE is the degradation of the modified surface showing up as the displacement of the current peak potential of the determined element, the distortion of the peak shape, and the emergence of additional peaks [195]. To make the GCE surface reproducible, it is prepared and cleaned by a great variety of methods such as mechanical polishing [108], treatment with reagents [76], electrochemical treatment by polarization at high anode potentials [36, 186], and exposure to microwaves or ultrasound [29, 40, 131]. Mechanical polishing of the surface with abrasive diamond or Al<sub>2</sub>O<sub>3</sub> powders or special polish cloths is in most common use. This surface treatment method is not only laborious and time-consuming, but what is the worst does not guarantee that the surface properties will be reproducible. This problem was attacked by development of automatic devices for cleaning of the solid electrode surface [116], but they have been used on a narrow scale because of their complexity and high cost. The original approach has been used [190] to modify GC with glassy carbon spheres covered by nanoparticles of precious metals and multiwalled nanotubes.

### Carbon-paste electrodes

In 1958, Adams described a new type of the carbon-paste electrode (CPE) for voltammetry. This electrode was

**Table 2** Modified carbon paste electrodes

Modifier <sup>a</sup>	Manner	Analyte	Detection limit (M)	Supporting electrolyte	Sweep mode <sup>b</sup>	Purge	Sample	Reference
Au <sub>nano</sub>	Ex situ	As (III)	$3\text{--}5\cdot 10^{-9}$	0.1 M HNO <sub>3</sub>	SQW ASV	–	BGD, mineral water	[202–203]
Au	Ex situ	As (III, V)	$4\cdot 10^{-8}$ As (III); $7\cdot 10^{-9}$ As (V)	1 M HClO <sub>4</sub> + 0.2 M HCl + $5\cdot 10^{-6}$ M Au (III)	LS ASV	+	River water	[204]
Au <sub>adatoms</sub>	In situ	Au (III)	$2\cdot 10^{-6}$	0.2 M H <sub>2</sub> SO <sub>4</sub>	CVA	–	Model mixtures	[205]
Au	In situ	Hg (II)	$2.5\cdot 10^{-10}$	0.1 M HNO <sub>3</sub> + 0.02 M KCl + $5\cdot 10^{-6}$ M Au (III)	DP ASV	–	Drinking water	[206]
Bi	In situ	Zn (II), Pb (II), Cd (II)	$1.5\cdot 10^{-8}$ (Pb)	0.1 M NaAc (pH 4.5) + $0.5\text{ mgL}^{-1}$ Bi (III)	SQW ASV	–	Model solutions	[207]
Bi	Ex situ	Cd (II), Pb (II)	$9\cdot 10^{-9}$ (Cd); $4\cdot 10^{-9}$ (Pb)	0.2 M acet. buff. (pH 4.25)	SQW ASV or DP ASV	–	Tap, sea waters	[208–209]
Bi <sub>2</sub> O <sub>3</sub> or Bi	Ex situ	Zn (II), Pb (II), Cd (II)	$4.4\cdot 10^{-8}$ (Cd); $2.4\cdot 10^{-8}$ (Pb)	0.1 M NaAc (pH 4.5)	DP ASV	–	Waters	[210–211]
Hg	In situ	Zn (II)	$1.3\cdot 10^{-7}$	0.1–0.2 M amm. buff. + $2\cdot 10^{-5}$ M Hg(NO <sub>3</sub> ) <sub>2</sub>	DP ASV	+	Drinking water	[212]
Hg	Ex situ	Cu (II), Pb (II), Cd (II)	$5\cdot 10^{-9}$	Ammonium acetate buff. (pH 4.5)	DP ASV	–	Fish muscles and water samples	[213]
Wax + Hg oxalate	Ex situ	Cu (II), Pb (II), Cd (II)	$3\cdot 10^{-9}$ (Cd)	0.1 M KCl or acet. buff. (pH 3.8)	DP ASV or LS ASV	+	Medicinal plants, tablets	[214]
Pt nanoparticles	Ex situ	Cu (II)	$3.9\cdot 10^{-9}$	0.1 M acet. buff. (pH 5.9)	LS ASV	–	Urine	[215]
DB18C6 (I), CuO (2)	Ex situ	Pb (II)	$2\cdot 10^{-9}$ (I); $2.5\cdot 10^{-9}$ (2)	0.1 M NaCl + $10^{-3}$ M 18C6 (I); 0.1 M NaCl (2)	DP ASV LS ASV	+	Soil, snow, air, waters	[216]
DB18C6	Ex situ	Cu (II), Pb (II)	$9.5\cdot 10^{-9}$ (Cu); $2\cdot 10^{-9}$ (Pb)	1 M NaAc (pH 5–6)	LS ASV, SQW ASV	+	Waste waters	[217]
Aza-crown compound	Ex situ	Ni (II), Co (II)	$4\cdot 10^{-8}$ (Ni); $1.2\cdot 10^{-7}$ (Co)	0.1 M NaCl (accumulation); 0.1 M KOH (sweep)	DP ASV (Co + Ni); DP CSV (Ni)	–	BGD	[218]
DB18C6 and its analogs	Ex situ	Au (III), Pt (IV), Pd (II)	$8\cdot 10^{-9}$ (Au); $3\cdot 10^{-7}$ (Pt); $2\cdot 10^{-8}$ (Pd)	0.1 M HCl	DP ASV	–	SS of ore	[219]
B15C5	Ex situ	Cu (II)	$8\cdot 10^{-7}$	Water-ethanol (40%) solutions	DP ASV	–	Strong drinks	[220]
Thiacrown compounds	Ex situ	Ag (I)	$5\cdot 10^{-7}$	NaClO <sub>4</sub> (accumulation); 0.1 M NaAc (sweep)	AVA	–	BGD	[221]
calix[4]arene	Ex situ	Cu (II)	$2\cdot 10^{-8}$	Acidified sample (accumulation); 0.1 M HCl (sweep)	DP ASV	–	Tap water	[222]
a-CD & b-CD	Ex situ	Pb (II)	$6.3\cdot 10^{-7}$ (Pb); $2.0\cdot 10^{-6}$ (Cd);	1 M HClO <sub>4</sub>	ASV	–	BGD	[223–

Table 2 (continued)

Modifier <sup>a</sup>	Manner	Analyte	Detection limit (M)	Supporting electrolyte	Sweep mode <sup>b</sup>	Purge	Sample	Reference
Zeolite	Ex situ	Cd (II), Hg (II)	$5 \cdot 10^{-8}$ (Hg)	0.05 M NaNO <sub>3</sub>	DP ASV	+	Dried tomato, bakosel capsule	[225]
		Cu (II)	$1.5 \cdot 10^{-8}$		DP ASV	–	Subsoil, sea waters	[226]
Silica	Ex situ	Cu (II)	$2 \cdot 10^{-9}$	0.1 M NH <sub>4</sub> OH	LS ASV, SQW ASV	–	Real Samples	[227–229]
Silica	Ex situ	Hg (II)	$2 \cdot 10^{-9}$	Solution pH 4–7	SQW ASV	–	Tap water	[230]
Silicas	Ex situ	Cu (II)	$3 \cdot 10^{-9}$	0.1 M HNO <sub>3</sub>	DP ASV	–	Natural waters	[231]
modified with	Ex situ	Hg (II)	$5 \cdot 10^{-10}$	Sample (pH 2) (accumulation); 0.05 M KNO <sub>3</sub> (sweep)	DP ASV	–	Ethanol fuel samples	[232]
AMT (1); AMT/DMG (2)	Ex situ/ in situ	Cu (II); Ni (II)	$3.1 \cdot 10^{-8}$ (Cu); $2 \cdot 10^{-9}$ (Ni)	Ethanol solution (accumulation); 0.1 M NH <sub>4</sub> Cl + $2.5 \cdot 10^{-3}$ M DMG (pH 9 for Ni)	DP ASV (1) DP CSV (2)	–		[233–234]
		Cd (II)	$1 \cdot 10^{-7}$	0.1 M phosphate buffer (pH 4)	DP ASV	+	Natural waters	[235]
thio-groups	Ex situ	Hg (II)	$(2.5-6.5) \cdot 10^{-8}$	HNO <sub>3</sub> (pH 3.0) (accumulation); 0.01 M KNO <sub>3</sub> (sweep)	DP ASV	–	BGD, natural water	[236–237]
Mercapto-groups	ex situ	Pb (II); Hg (II)	$2.4 \cdot 10^{-9}$ (Pb); $1.5 \cdot 10^{-8}$ (Hg)	0.2 M HNO <sub>3</sub>	SQW ASV	–	BGD	[238]
		Hg (II)	$1 \cdot 10^{-6}$	pH 1 (accumulation); 0.1 M HCl + 5% thiourea (sweep)	DP ASV	–	BGD	[239]
CPA	ex situ	U (VI)	$1 \cdot 10^{-7}$	0.05 M CH <sub>3</sub> COONa (pH 5) (accumulation); 0.2 M HNO <sub>3</sub> (sweep)	DP ASV	–	BGD	[240]
Monsil	Ex situ	Cd (II); Pb (II); Cu (II)	$8.9 \cdot 10^{-8}$ (Cd); $4.8 \cdot 10^{-8}$ (Pb); $1.6 \cdot 10^{-7}$ (Cu)	0.1 M NaClO <sub>4</sub> + 1.5 M HClO <sub>4</sub> (Hg, Ag, Pb); 0.1 M KCl + 1.0 M HCl (Cu)	SQW ASV	–	BGD	[241]
		Hg (II); Ag (I); Pb (II); Cu (II)	$4 \cdot 10^{-4}$ (Cu); $1 \cdot 10^{-3}$ (Ag, Hg); $5 \cdot 10^{-4}$ (Pb)		CVA	+	BGD	[242]
ZrPH	Ex situ	Cd (II)	$2 \cdot 10^{-9}$	0.05 M B-R buff. (pH 3) (accumulation); 0.1 M citrate buff. (pH 3.5) (sweep)	DP ASV	–	Artificial synthetic samples	[243]
Vermiculite	Ex situ	Cu (II)	$5 \cdot 10^{-9}$	0.04 M B-R buff. (accumulation); 0.1 M NaNO <sub>3</sub> + 0.02 M B-R buff. (sweep)	SQW ASV DP ASV	–	SRM 1643b (SS)	[244–245]
Vermiculite	Ex situ	Cu (II); Ag (I)	$1.9 \cdot 10^{-5}$ (Ag); $3.1 \cdot 10^{-6}$ (Cu)	0.01 M NaClO <sub>4</sub>	DP ASV	–	BGD	[246]
Vermiculite	Ex situ	Hg (II); Ag (I)	$5.7 \cdot 10^{-8}$ (Hg); $6.3 \cdot 10^{-8}$ (Ag)	B-R buff. – pH 7 (Hg), pH 6 (Ag) (accumulation); B-R buff. (pH 5) + 0.05 M NaNO <sub>3</sub> (sweep)	SQW ASV	–	Model solutions	[247]
Montmorillonite	Ex situ	Cu (II)	$4 \cdot 10^{-8}$	NaAc (pH 5.5)	DP ASV	–	Model solutions	[248]
Montmorillonite	Ex situ	Bi (III)	$1 \cdot 10^{-10}$	0.1 M HCl	DP ASV	–	Water, nickel metal	[249]

Montmorillonite	Ex situ	Hg (II)	$1 \cdot 10^{-10}$		0.1 M tartaric acid	ASV	–	BGD	[250]
	Ex situ	Hg (II)	$5 \cdot 10^{-8}$		1 M KCl (pH 2)	DP ASV	–	Natural water	[251]
	Ex situ	Fe (III)	$3.6 \cdot 10^{-6}$		0.05 M KCl (pH 3.2)	DP CSV	–	BGD	[252]
TZT-HDTPA-clay	Ex situ	Hg (II)	$5 \cdot 10^{-10}$		Sample (pH 2–5) (accumulation); 0.05 M KNO <sub>3</sub> (sweep)	DP ASV	–	Natural water	[253]
Dowex CGC241	Ex situ	Cu (II)	$6.25 \cdot 10^{-5}$		0.1 M CH <sub>3</sub> COONa (pH 6.8)	DP CSV	+	Model solutions	[254]
Dowex 50W-8X	Ex situ	Cu (II)	$1 \cdot 10^{-7}$		0.01 M KNO <sub>3</sub> (accumulation); 0.1 M HCl (1 M KNO <sub>3</sub> ) (sweep)	DP ASV	–	Waste waters	[255]
Amberlite IRS 718	Ex situ	Cd (II)	$4.4 \cdot 10^{-8}$		1 mM amm. buff. (accumulation); 0.1 M HCl (sweep)	LS ASV	–	River waters	[256]
Dyolite GT-73	Ex situ	Hg (II); CH <sub>3</sub> Hg <sup>+</sup> (I)	$2.0 \cdot 10^{-8}$ (Hg); $9.4 \cdot 10^{-9}$ (CH <sub>3</sub> Hg <sup>+</sup> )		0.1 M HCl	CV	–	River waters	[257]
Ion-exchange resin	Ex situ	Cu (II); Pb (II); Hg (II)	$2.4 \cdot 10^{-7}$ (Cu); $1.1 \cdot 10^{-7}$ (Pb); $5.0 \cdot 10^{-8}$ (Hg)		0.1 M KNO <sub>3</sub> + $5 \cdot 10^{-3}$ M CH <sub>3</sub> COOH	DP ASV	–	Drinking water	[258]
Humic acids	Ex situ	Pd (II)	$9.4 \cdot 10^{-8}$		0.1 M B-R buff. (pH 2.8) (accumulation); 1.0 M HCl (sweep)	LS ASV	–	Catalysts, precious metals	[259]
Humic acids	Ex situ	Pb (II); Cu (II); Hg (II)	$4.8 \cdot 10^{-9}$ (Pb); $7.9 \cdot 10^{-9}$ (Cu); $8.0 \cdot 10^{-9}$ (Hg)		0.1 M KNO <sub>3</sub>	DP ASV	+	SRM 2670 (SS), urine	[260]
Humic acids + EDA	Ex situ	Au (III)	$5 \cdot 10^{-8}$		0.35 M HNO <sub>3</sub> (accumulation); 0.8 M HCl (sweep)	DP ASV	–	Ores	[261]
Humic acids/amides	Ex situ	Hg (I; II)	$5 \cdot 10^{-8}$		0.1 M H <sub>2</sub> SO <sub>4</sub> (accumulation); 0.5 M H <sub>2</sub> SO <sub>4</sub> (sweep)	LS ASV	–	River waters	[262]
Soils	Ex situ	Cu (II)	$1.2 \cdot 10^{-5}$		0.04 M B-R buff. + 0.1 M KNO <sub>3</sub>	DP ASV	+	Model solutions	[263]
HSF-Na	In situ	Ag (I)	$2.5 \cdot 10^{-12}$		0.02 M NaAc + $8.3 \cdot 10^{-5}$ M HSF-Na + 3 mM EDTA	DP ASV	+	Tap water	[264]
TTCP	In situ	Ag (I)	$1 \cdot 10^{-4}$		0.2 TBAP + $1 \cdot 10^{-3}$ TTCP	CV	–	BGD	[265]
BPG	In situ	Bi (III)	$5 \cdot 10^{-10}$		0.3 M HCl + $2.0 \cdot 10^{-5}$ M BPG	ASV	+	Waters, hair	[266]
ARS	In situ	Cu (II)	$1.6 \cdot 10^{-10}$		0.04 M B-R buff. (pH 4.56) + $3.6 \cdot 10^{-5}$ M ARS + $1.6 \cdot 10^{-3}$ M K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	SD CSV	–	Natural water, soil	[267]
ARS	In situ	Zr (IV)	$1 \cdot 10^{-10}$		0.1 M acetic acid + 0.08 M KHP (pH 4.8) + $4 \cdot 10^{-6}$ M ARS	SD CSV	–	Ore samples	[268]
ARS + CTAB	In situ	Ce (IV)	$6 \cdot 10^{-10}$		0.1 M HAc-NaAc + 0.2 M KHP (pH 5) + $2 \cdot 10^{-6}$ M ARS + $6 \cdot 10^{-5}$ M CTAB	SD CSV	–	Cast iron samples	[269]
CTAB	In situ	Ti (IV); V (V); Mo (VI)	$2.0 \cdot 10^{-9}$ (Ti); $1.4 \cdot 10^{-9}$ (V); $4.2 \cdot 10^{-10}$ (Mo)		0.01 M oxalic acid + x mM CTAB; x=0.1 (Ti); 0.25 (V); 0.75 (Mo)	DP ASV	+	Rock, fuel, steel	[270–271]
CTAB, Septonex	In situ	Os (IV); Pt (IV); Jr (IV)	$5 \cdot 10^{-9}$ (Os); $1 \cdot 10^{-6}$ (Pt, Jr)		0.1 M acet. buff. + 0.15 M NaCl + $1 \cdot 10^{-5}$ M CTAB or Septonex (pH 4.5–6)	DP CSV	+	Industrial waste water	[272–273]

**Table 2** (continued)

Modifier <sup>a</sup>	Manner	Analyte	Detection limit (M)	Supporting electrolyte	Sweep mode <sup>b</sup>	Purge Sample	Reference
EDTA	In situ	Fe (III)	$2 \cdot 10^{-7}$	0.01 M KCl + $3 \cdot 10^{-4}$ M EDTA (pH 3.0)	DP CSV	+	River and tap waters [274]
DAN	In situ	Se (IV)	$1.3 \cdot 10^{-7}$	0.1 M KCl (pH 2) + $1 \cdot 10^{-4}$ M DAN (accumulation); 0.1 M HNO <sub>3</sub> + 0.1 M KNO <sub>3</sub> (sweep)	LS CSV	+	Natural, waste waters [275]
Thioridazine	In situ	Pd (II)	$4.7 \cdot 10^{-9}$	0.08 M HCl + $75 \text{ mgL}^{-1}$ Thioridazine	DP ASV	+	Drinking water [276]
Mo-GGPA, Mo-SA	In situ	Ge (III); Si (IV)	$0.17 \cdot 10^{-8}$ (Ge); $0.09 \cdot 10^{-8}$ (Si)	0.1 M citrate buff. (pH 2.5) + Mo-GGPA (Mo-SA)	DP CSV	–	Semiconductors, refined waters [277–279]
PEI	In situ	Ag (I); Hg (II); Cu (II); Pb (II); Cd (II)	$0.9 \cdot 10^{-6}$ (Ag); $1.1 \cdot 10^{-6}$ (Hg, Cu); $8.0 \cdot 10^{-7}$ (Pb); $8.4 \cdot 10^{-7}$ (Cd)	0.1 M KCl (0.1 M KNO <sub>3</sub> ) + 2% PEI (pH 3 for Pb, Cd and pH 2 for Cu)	LS ASV	–	Tap water [280–283]
IDA	Ex situ	Pb (II)	$25.4 \text{ } \mu\text{g/kg}$	(pH 6) (accumulation); acet-ammonium buff. (pH 3) (sweep)	DP ASV	–	SS of water [284]
8HXQ	Ex situ	Tl (I)	$4.9 \cdot 10^{-9}$	0.01 M B-R buff. (pH 7.96) (accumulation); 0.2 M amm. buff. (pH 10) (sweep)	DP ASV	–	USEPA SS (WP 386) [285]
2-methyl-8HXQ	Ex situ	Cu (II)	$3.3 \cdot 10^{-9}$	0.05 M KSCN + 0.05 M KSCN + B-R buff. (sweep)	DP ASV	+	SS [286]
2,3-Dicyano-1,4-naphthoquinone	Ex situ	Ag (I)	$5 \cdot 10^{-8}$	0.1 M KNO <sub>3</sub>	LS CSV	–	BGD [287]
N-p-CPCHA	Ex situ	Cd (II)	$5.5 \cdot 10^{-9}$	0.3 M NH <sub>4</sub> Cl (pH 5)	DP ASV	–	Mineral and drinking waters [288]
N-p-CPCHA	Ex situ	Pb (II)	$10^{-8} - 10^{-9}$	0.3 M CH <sub>3</sub> COONa (pH 6)	DP ASV	–	Drinking water [289]
N-p-CPCHA	Ex situ	Co (II)	$3.3 \cdot 10^{-7}$	0.2 M CH <sub>3</sub> COONa (pH 6)	DP ASV	–	Vitamin B <sub>12</sub> [290]
Dithizone	Ex situ	Pb (II)	$8 \cdot 10^{-8}$	Sample pH 12 (accumulation); 0.1 M HCl (sweep)	DP ASV	–	River water [291]
Thiohydrazine	Ex situ	Cu (II)	$8 \cdot 10^{-9}$	0.1 M HCl	CV	–	River waters [292]
BBTSC	Ex situ	Hg (II)	$4 \cdot 10^{-8}$	0.01 M KNO <sub>3</sub> (accumulation); 0.1 M HCl (sweep)	SQW ASV	–	River waters [293]
FTHD	Ex situ	Cd (II)	$5 \cdot 10^{-10}$	B-R buff. (pH 4)	DP ASV	–	Model solutions [294]
DPCO	Ex situ	Hg (II)	$5 \cdot 10^{-9}$	0.1 M KSCN (pH 2)	DP ASV	–	BGD [295]
PTL derivative	Ex situ	Cu (I)	$5 \cdot 10^{-9}$	0.5 M CH <sub>3</sub> COONa (pH 6)	DP ASV	–	CO NBS 1643 [296]
PTL + nafion	Ex situ	Fe (II)	$3 \cdot 10^{-8}$	B-R buff. (pH 4.5)	DP CSV	–	Waters, SS of alloys [297]
Diacyldioxime	Ex situ	Pb (II); Cd (II)	$1 \cdot 10^{-8}$ (Pb); $4 \cdot 10^{-8}$ (Cd)	0.1 M NaH <sub>2</sub> PO <sub>4</sub>	DP ASV	–	Natural waters [298]
PAN	Ex situ	Mn (II; VII)	$6.9 \cdot 10^{-9}$ Mn (II)	Phosphate-borate buffer (pH 8.7)	DP CSV	+	SS, sea water [299]

TDPTA	Ex situ	Co (II)	$5.0 \cdot 10^{-10}$	(accumulation); amm. buff. (pH 9.4) (sweep)	DP CSV	+	Drinking water	[300]
Thiourea derivative	Ex situ	Ag (I)	$9.3 \cdot 10^{-8}$	0.1 M $\text{NH}_4\text{Cl}$ (pH 4.95)	LS ASV	–	BGD	[301]
Chelate P	Ex situ	Cu (II)	$3 \cdot 10^{-8}$	1 M $\text{NaClO}_4$ (pH 3.0) Sample (accumulation); 1.0 M $\text{HNO}_3$ (sweep)	DP ASV	–	River water	[302]
Cupron	Ex situ	Cu (II)	$4.7 \cdot 10^{-9}$	amm. buff (pH 8.5) (accumulation); 1.0 M $\text{HNO}_3$ (sweep)	LS ASV	–	Anodic mud, polluted water	[303]
Glyoxal derivative	Ex situ	Hg (II); Ag (I)	$1 \cdot 10^{-9}$ (Hg); $1 \cdot 10^{-10}$ (Ag)	0.1 M $\text{NaAc}$ (pH 5) (accumulation); 0.1 M $\text{KNO}_3$ (sweep)	DP ASV	+	SRM 2670 (SS)	[304]
Phenylfluorone	Ex situ	Sb (III)	$8.2 \cdot 10^{-9}$	0.5 M $\text{HCl}$	DP ASV	+	Hair, soil	[305]
PPDA	Ex situ	Pb (II)	$1 \cdot 10^{-9}$	0.1 M $\text{KNO}_3$ (accumulation); 0.1 M $\text{HCl}$ (sweep)	DP ASV	–	Sea waters	[306]
Zn-DDC	Ex situ	Hg (II)	$8 \cdot 10^{-10}$	0.1 M $\text{HClO}_4$ (accumulation); 0.1 M $\text{KSCN} + 0.01$ M $\text{HClO}_4$ (sweep)	DP ASV	+	USEPA SS (WP 386), urine	[307]
DMG + glycerol	Ex situ	Hg (II); Ni (II); Co (II); Pd (II)	$10^{-8}$	Buffer (pH 4.8)	CSV		Rice, tea, hair	[308]
TBP	Ex situ	Zn (II); Ga (III)	$2 \cdot 10^{-6}$	7 M $\text{HCl}$ (accumulation); 0.5 M ethanolamine + 0.2 M TEA-Br (sweep)	CVA	–	Model mixtures	[309]
Morin	Ex situ	Zr (IV)	$1 \cdot 10^{-8}$	2.2 M $\text{HCl}$	SD ASV	–	Ore	[310]
Lichen	Ex situ	Pb (II); Cu (II)	$2 \cdot 10^{-5}$ (Pb)	0.02 M phosphate buffer (Pb); 0.02 M $\text{NaAc}$ (Cu)	DP ASV	+	–	[311]
Lichen	Ex situ	Pb (II)	$1 \cdot 10^{-8}$	$\text{NaAc}$ with ionic force 0.01 (accumulation); $\text{NaAc}$ with ionic force 0.7 (sweep)	DP ASV	–	Natural and drinking waters	[312]

For other abbreviations see Table 1.

<sup>a</sup> *HSF-Na* Sodium heptyl sulfonate, *TTCP* 2,5,8-trithio[9]-*n*-cyclophane, *BPG* brompyrogallol, *DAN* diammonaphthalene, *Mo-GGPA* molybdenum-germanium heteropolyacid, *Mo-SA* molybdsilicic acid, *PEI* polyethylenimine, *IDA* iminodiacetate, *DB18C6* dibenzo-18-crown-6, *B15C5* benzo-15-crown-5,  $\alpha$ -*CD* and  $\beta$ -cyclodextrins, *CFA* carbamoyl phosphonic acid, *AMT* 2-aminothiazole, *ZrPH* zirconium phosphate, *KHP* potassium biphthalate, *TZT-HDTA-clay* 2-thiazoline-2-thiol-hexadecyltrimethylammonium-clay, *N-p-CPCA* chlorophenyl cinnamohydroxamic acid, *BBTSC* benzylbisthiosemicarbazone, *FTHD* 1-furoylthiureas, *DPCO* diphenylcarbazone, *PTL* 1,10-phenanthroline, *TDPTA* 2,4,6-tri(3,5-dimethylpyrazolyl)-1,3,5-triazine, *PPDA* poly-*n*-phenylenediamine, *TBP* tri-*n*-butylphosphate

<sup>b</sup> *CVA* Cathodic voltammetry, *SD* second derivative of voltammogram



conceived because despite good performance capabilities of mercury electrodes with respect to the adsorptive concentration of inorganic ions [196–198], they have some limitations at positive potential range, while many solid electrodes, which are operable over a wide interval of potentials, cannot selectively sorb the required component of the system. Adams' idea was not overlooked by other investigators, and in 1964, Kuwana et al. performed research making the first contribution to the advancement of chemically modified carbon-paste electrodes, which are described in the reviews [199–201].

CPE is made of a homogenized paste of fine-dispersed coal and a water-immiscible binding liquid. Paraffin, petrolatum, or polychlorotrifluoroethylene oils, silicon fluid, dioctylphthalate,  $\alpha$ -bromonaphthalene, tricresyl phosphate, and other materials can be used as the binding liquid. Two types of CPE pastes are available: dry (0.3–0.5 ml of the binding liquid per 1 g of the carbon powder) and wet (0.5–0.9 ml of the binding liquid per 1 g of the carbon powder) pastes. CPE can bear a high residual current caused by oxygen admixed to the paste with carbon powder particles. The residual current can be eliminated if the preheated carbon powder is mixed with wax, paraffin, or petrolatum oil in the nitrogen atmosphere or a lipophilic paste fluid (tricresyl phosphate) is added. The detection limit (LOD) of many inorganic and organic substances on CPE generally is  $1 \cdot 10^{-9}$  M. LOD is frequently decreased by activation of the electrode at high negative or positive potentials. The anode activation of the electrode is most efficient because interfering organic substances can be removed from the surface in this case. Sometimes the electrode is “shaken up” through the cyclic polarization between large negative and positive potentials.

When compared to other carbon-containing electrodes, CPE has a well-developed surface with a high adsorptivity of various substances. This property of CPE is used successfully in voltammetry for the modification and the adsorptive accumulation of substances to be measured. A modifier can be immobilized on CPE by several means including sorption, covalent binding, dissolution of a lipophilic modifier in the paste fluid, and direct mixing with the carbon paste. Direct mixing of a modifier with the paste is used most frequently. This modification procedure is very simple: a modifier is added to the paste in the dry form or diluted in a small amount of an organic solvent making the paste more homogeneous. Other methods of the modifier immobilization are used least often. The depolarizer is concentrated on the modified CPE surface through adsorption, chemical, or electrostatic interaction of the element to be measured and the modifier. CPE is modified by various organic substances such as aromatic oxycarboxylic acids, aromatic amine and diimine compounds, azocompounds, dyes, thiocompounds, triazines, and quino-

lines. In addition to the main hydrocarbon chain, molecules of these organic compounds include nitrogen, sulfur, and oxygen atoms, aromatic and aliphatic cycles containing unbound  $\pi$ -electrons, which can interact, on one hand, with the electrode surface and, on the other hand, with the analyte ensuring a high surface adsorption and strong binding to the substance to be determined.

Every so often, the analyte is concentrated on modified CPE with the circuit open using extraction, sorption, ion exchange, and formation of ion pairs. The measurement stage can be accomplished in another electrolyte. As the electrolyte is replaced, it is possible to optimize the measurement parameters (pH, the ionic force, and the potential) and eliminate the interference of other components of the test solution. Dependences of the current peak of the element to be determined on the concentration and the accumulation time on CPE are flattened-out curves because all functional groups of the modifier are saturated.

Table 2 gives examples of specific applications of modified CPE for the voltammetric determination of metal ions [202–312]. Sometimes CPE is modified by films of metals and their oxides [202–213, 215–216]. The electrode is modified most frequently by crown compounds [216–221], calixarenes [222], cyclodextrins [223–225], non-functionalized and functionalized silica [226–243], clay minerals (vermiculite and montmorillonite) [244–253], ion exchangers in the form of artificial resins [254–258, 258–262], natural humic acids and soils [259–263], organic [264–310], and bioactive compounds [311–312].

Electrodes based on silica with self-organizing monolayers, for example, mesoporous silica modified by acetamide of the phosphonic acid provide accumulation and measurement of Cu, Pb, Cd, and U [240–241]. CPE modified by biocatalysts, which are constituents of  $\alpha$ - and  $\beta$ -cyclodextrins [223–225] or natural lichens [311–312] are used for measurement of ions of heavy metals.

Solid depolarizers can be studied after their direct infusion to CPE, which has been called the carbon-paste electroactive electrode (CPEE). The CPEE methodology was recognized to be also suitable for insoluble electroactive compounds. The first studies of metals, metal oxides, chalcogenides, salts, and other compounds by CPEE methodology were reviewed by Brainina et al. [313]. Electrochemical transformations taking place on CPEE provide information about the electrochemical activity of solid compounds, their stoichiometry, the oxidized state of elements, the morphology (the size and the shape of particles, crystal defects), the catalytic activity, etc. The CPEE methodology significantly increased the scope of electrochemistry to poorly conducting and insoluble solids. CPEE is used to analyze lead sulfides, magnetite, oxides of silver, tin, copper, and iron, bromides of rare-earth elements, nickel-containing compounds and other solids,



e.g., ceramics and glasses [314–318]. A comprehensive review [319] is dedicated to the electrochemical analysis of solids.

## Conclusion

Considering the above numerous examples of the electrochemical study and determination of various elements and compounds, it can be concluded that the modification of the surface of solid electrodes by a variety of methods and substances considerably extends the capabilities of voltammetry and ensures a highly sensitive and selective determination of a wide range of elements traces.

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